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Reaction Mechanisms

The σ-CAM Mechanism: σ Complexes as the Basis of σ-Bond Metathesis at Late-Transition-Metal Centers**

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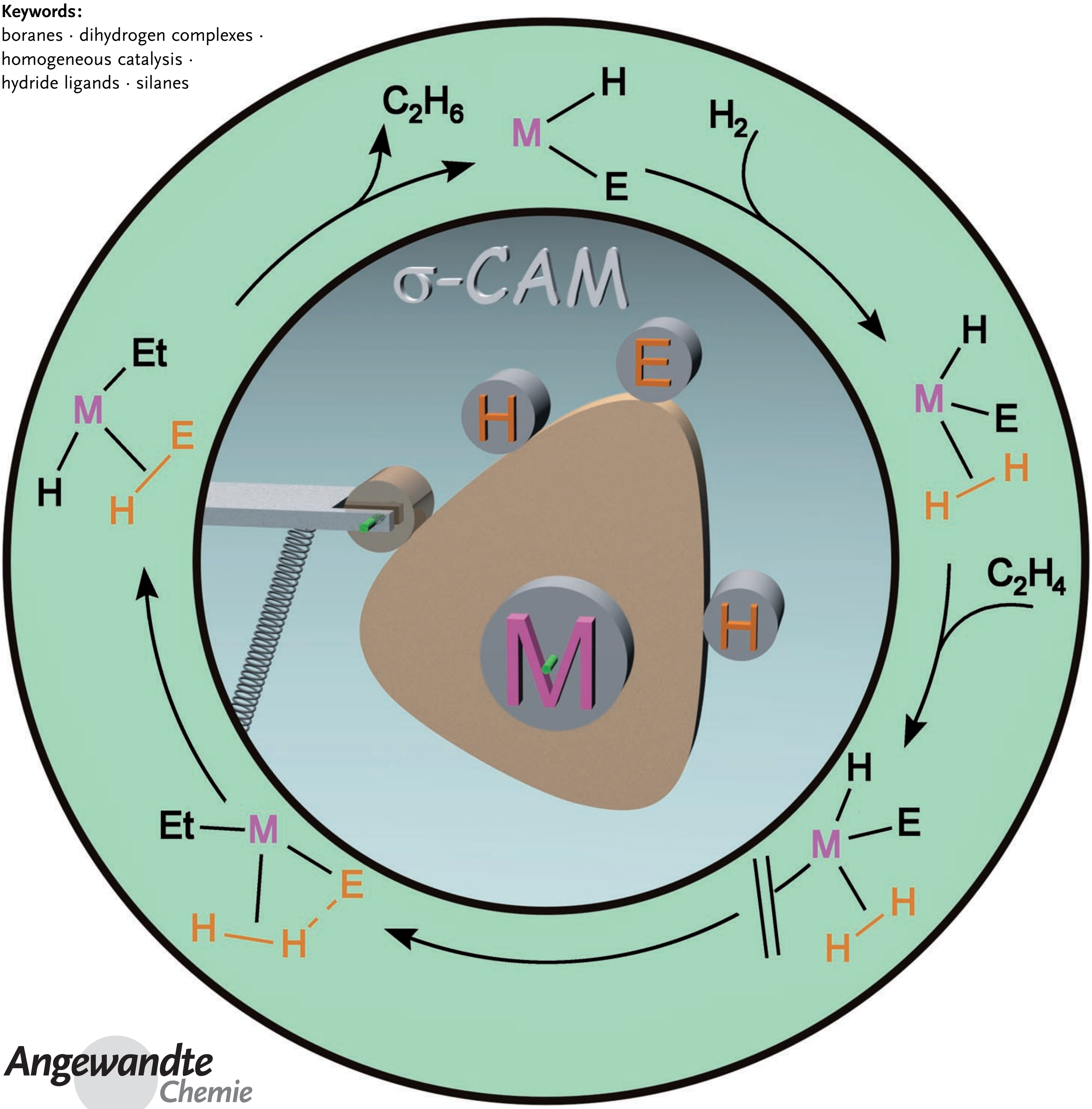

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Complexes in which a σ-H–E bond (E = H, B, Si, C) acts as a two-electron donor to the metal center are called σ complexes. Clues that it is possible to interconvert σ ligands without a change in oxidation state derive from C–H activation reactions effecting isotope exchange and from dynamic rearrangements of σ complexes (see Frontispiece). Through these pathways, metathesis of M–E bonds can occur at late transition metals. We call this process σ-complex-assisted metathesis, or σ-CAM, which is distinct from the familiar σ-bond metathesis (typical for d^0 metals and requiring no intermediate) and from oxidative-reductive elimination mechanisms (inherently requiring intermediates with changed oxidation states and sometimes involving σ complexes). There are examples of σ-CAM mechanisms in catalysis, especially for alkane borylation and isotope exchange of alkanes. It may also occur in silylation and alkene hydrogenation.

From the Contents

1. Introduction

The oxidative addition of H_2 at a transition-metal center to form $M(H)_2$ is one of the most fundamental reactions in chemistry. However, there is an alternative mode of coordination in which H_2 binds to the metal center while retaining the H–H bond, denoted as a dihydrogen complex or $M(\eta^2\text{-H-H})$. The term σ complexes is used to describe metal complexes containing a ligand in which a σ bond, usually H–E (E = nonmetal) acts as a two-electron donor to the metal center, resulting in a three-center bond (Figure 1).[1–3]

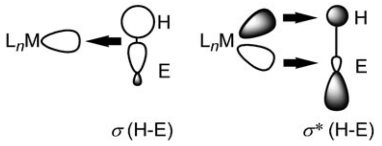
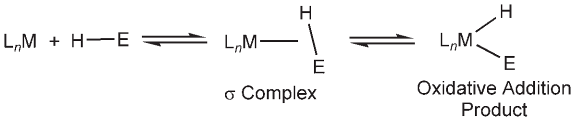


Figure 1. General bonding scheme for σ complexes.

Dihydrogen complexes form the best-known group of σ complexes in which H_2 is bound to the metal center sideways (η^2). There are also crystallographically characterized examples with E = Si and E = B, termed η^2-silane and η^2-borane complexes. There have been substantial recent advances in the detection of the carbon analogues in which alkanes are coordinated through η^2-C–H bonds.[4,5] Two publications report X-ray evidence for a coordinated alkane to a metal center, namely a heptane–iron adduct in a double-A-frame porphyrin,[6] and the coordination of various alkanes to an electron-rich uranium(III) center.[7] The intramolecular analogue with a pendant alkyl group is well-known for E = C under the specific name of agostic complexes, but is not the topic of this Review. When a metal fragment such as $\{W(CO)_3(\text{phosphine})_2\}$ binds a ligand as a σ complex, there is no change in oxidation state. There is abundant evidence that σ complexes may act as reaction intermediates in the oxidative addition of H–E (E = H, C, B, Si) and its microscopic reverse, reductive elimination, especially for d^8-d^6-d^8 (or d^6-d^8-d^6) sequences (Scheme 1).[1,2,4,8–14]



Scheme 1. Oxidative addition with an intermediate σ complex.

A sequence of such reactions results in ligand exchange at the metal center and formation of new E–H bonds. Scheme 2a illustrates conversion of M–E to M–E′ by oxidative addition of H–E′ and reductive elimination of H–E. Scheme 2b shows an alternative sequence starting with $M(H)_2E$ where reductive elimination of dihydrogen is followed by oxidative addition of H–E′, yielding an M(E)(E′)H unit. If E and E′ are different isotopes of the same element or if H is replaced by D, such processes lead to isotope exchange. Scheme 2c shows isotope exchange in a methyl hydride complex to form an intermediate σ complex. The first step to form the σ complex is usually termed *reductive coupling* while the reverse is referred to as *oxidative cleavage*. These terms also apply to the corresponding steps in Scheme 2a, b.

Such reactions play a major role in stoichiometric and catalytic functionalization of a variety of substrates as

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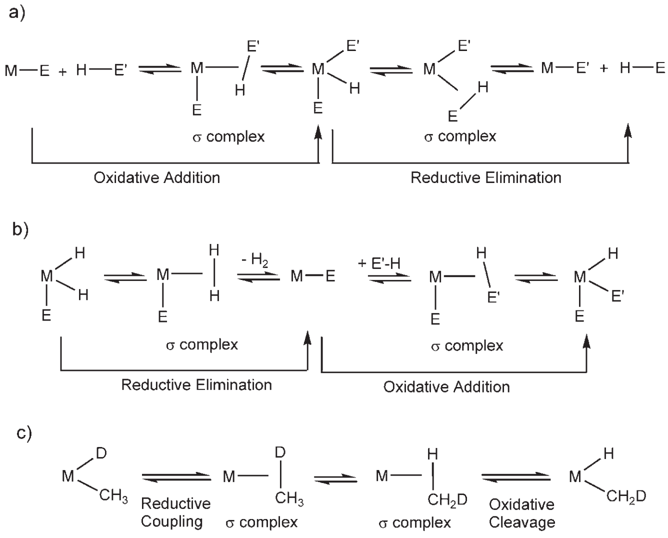
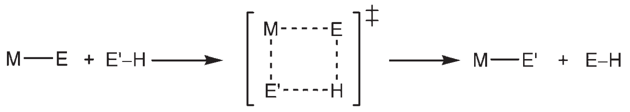
[**] σ-CAM: σ-complex-assisted metathesis.



Scheme 2. a) Metathesis reactions by oxidative addition and subsequent reductive elimination; b) metathesis reactions by reductive elimination and subsequent oxidative addition with intermediate σ complexes; c) isotope exchange in a methyl hydride complex by reductive coupling to an intermediate σ-CH_4 complex with subsequent oxidative cleavage.

exemplified, for instance, by Bergman and co-workers' studies of alkane C–H bond activation.[8–10,14] They are also very important in isotope-exchange reactions that often provide the decisive evidence for the existence of the σ complexes. Such processes are considered in detail for rhodium complexes by Jones and for platinum complexes by Lersch and Tilset.[11–13] As an alternative to sequences involving oxidative addition and reductive elimination, pathways involving σ-bond metathesis have often been proposed;[8] such pathways allow ligand (or isotope) exchange at a constant oxidation state. The ideas of σ-bond metathesis involving a four-center transition state stem from the chemistry of d^0 metals, for which oxidative addition is impossible (Scheme 3).[8,15,16]

In this Review, we explore how modern knowledge of isolable σ complexes, particularly with silane and borane ligands, allows σ-bond metathesis to be adapted to the context of late transition metals. Following a summary of the structural features of σ complexes, especially those with two σ ligands, we demonstrate that dynamic rearrangements of σ complexes illustrate the fundamental ability of σ complexes to interchange hydrogen with one another, thereby generating new σ ligands. When a complex contains a hydride ligand and one or two σ ligands, NMR spectra typically reveal dynamic exchange between all the different hydrogen atoms of the hydride and σ ligands. These dynamic processes provide the clue that it is possible to interconvert σ ligands without a change in oxidation state as shown in the example in Equation (1), in which a hydrido σ-silane complex is converted to a silyl dihydrogen complex.



Scheme 3. σ-Bond metathesis.

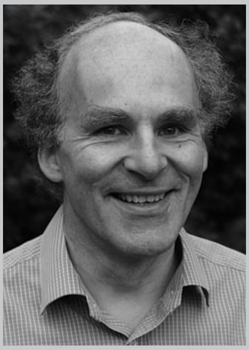
$$[MH(\eta^2\text{-H-SiR}_3)] \rightarrow [M(SiR_3)(\eta^2\text{-H-H})] \qquad (1)$$

This step can be combined with initial coordination of silane and ultimate release of H_2 to complete a metathesis sequence [Eq. (2)]. We call this process σ-complex-assisted metathesis, or σ-CAM.

$$\begin{aligned} &MH + HSiR_3 \rightarrow [MH(\eta^2\text{-H-SiR}_3)] \rightarrow \\ &[M(SiR_3)(\eta^2\text{-H-H})] \rightarrow M(SiR_3) + H_2 \end{aligned} \qquad (2)$$

In consequence, rearrangements of pairs of σ ligands can lead to ligand metathesis—we show that this class of mechanism is distinct from traditional σ-bond metathesis and designate it the σ-CAM mechanism.[+] Finally, we show that catalytic cycles can operate through a sequence of such rearrangements, providing a route to functionalization at constant oxidation state that involves a series of discrete σ complexes as intermediates.

[+] A cam is described in the *Shorter Oxford Dictionary* as "a projecting part of a wheel, etc. in machinery used to impart reciprocal or variable motion to another part with which it makes sliding contact as it rotates." In the σ-CAM mechanism, the metal acts as the cam on which the ligands move.



Robin Perutz obtained his PhD in 1974 on metal carbonyl complexes under J. J. Turner in Cambridge and Newcastle, where he established the existence of one of the first alkane σ complexes. After periods in Muelheim, Edinburgh, and Oxford, he moved to York in 1983, where he has been Professor of Chemistry since 1991. His interests encompass many aspects of the reaction mechanisms, photochemistry, spectroscopy, and synthesis of organotransition-metal and metal-hydride complexes, as well as C–F activation and more recently supramolecular photochemistry and ultrafast IR spectroscopy.

Sylviane Sabo-Etienne, born in France in 1956, received her "Doctorat d'Etat" in 1984 from the Université Paul Sabatier, Toulouse, with Prof. Danièle Gervais in heterobimetallic complexes. After research stays in Brest (with Prof. Hervé des Abbayes; iron carbonylation), Chapel Hill (Prof. Maurice Brookhart; Rh-catalyzed acrylate dimerization), and again Toulouse (Dr. Bruno Chaudret; polyhydrides), she was promoted to "Directrice de Recherche CNRS" in 1997. Her research interests include various aspects of coordination chemistry and catalysis with emphasis on σ complexes, hydrogen transfer, and C–H activation.

2. σ-Bond Metathesis at d^0 Centers

The idea of σ-bond metathesis was developed for complexes of d^0 configuration, especially of the type $[Cp_2MR]$ ($Cp = \eta^5\text{-}C_5H_5$; M = Sc, Ln) and $[Cp_2MR_2]$ (M = Ti, Zr, Hf). The metal centers are in their highest possible oxidation states and are unable to change to lower states, thus excluding reductive elimination and oxidative addition mechanisms. Extensive experimental and theoretical studies have led to the concept of the general four-center transition state (Scheme 3).[8–10,15–17] A more specific example illustrates a prototype reaction treated by experiment[18] and theory.[19] Reaction of D_2 with $[(\eta^5\text{-}C_5Me_5)_2ScH]$ leads to $[(\eta^5\text{-}C_5Me_5)_2ScD]$; theoretical analysis of the reaction of H_2 with the C_5H_5 analogue reveals a weakly bound dihydrogen adduct as an intermediate and a kite-shaped transition state (Figure 2).

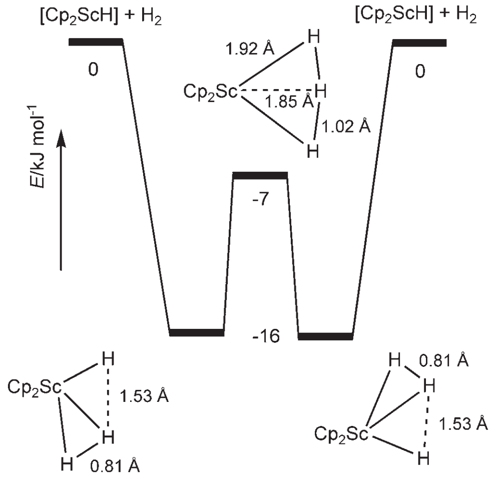
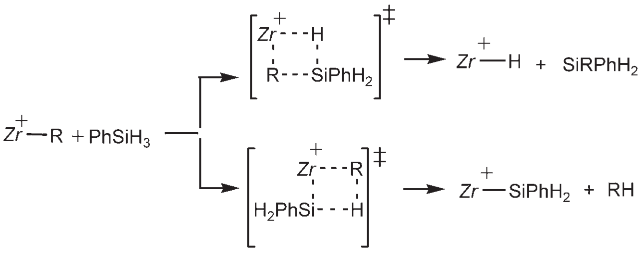


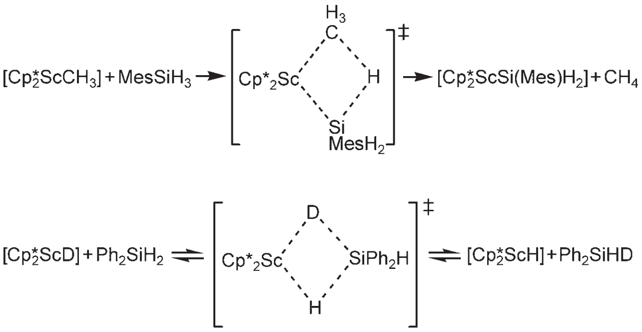
Figure 2. Calculated energy profile for σ-bond metathesis of H_2 with $[Cp_2ScH]$ according to reference [19].

Two modern examples illustrate the power of such reactions. Wu and Jordan have treated stabilized $[Cp_2Zr(alkyl)]^+$ ions with phenylsilane and have shown that two pathways operate according to the orientation adopted by the phenylsilane in the transition state (Scheme 4).[20] One pathway leads to $[Cp_2ZrH]^+$ and $SiRPhH_2$, while the other leads to $[Cp_2ZrSiPhH_2]^+$ and RH. Reactions of d^0 complexes through σ-bond metathesis can lead to productive catalysis, as exemplified by the coupling of alkenes and substituted pyridines catalyzed by $[Cp_2ZrMe]^+$.[21]



Scheme 4. σ-Bond metathesis reactions of phenylsilane at zirconocene complexes. *Zr* = $\{Cp_2Zr\}$.

Sadow and Tilley have treated $[Cp^*_2ScMe]$ ($Cp^* = \eta^5\text{-}C_5Me_5$) with mesitylsilane to form $[Cp^*_2Sc\{Si(Mes)H_2\}]$ and methane. In a related process, $[Cp^*_2ScD]$ reacts with Ph_2SiH_2 to form $[Cp^*_2ScH]$ and Ph_2SiHD (Scheme 5).[15] DFT calculations for these reactions generate transition states in full accord with the four-center scheme. Intriguingly, the calculations show an additional α-agostic interaction of a C–H bond, but the experimental isotope effects do not establish whether this is significant. In a third variant, $[Cp^*_2Sc\{Si(Mes)H_2\}]$ reacts with methane to form both $[Cp^*_2ScMe]$ and $[Cp^*_2ScH]$ and the corresponding silanes. Looking more widely, transition states involving Sc in any combination or orientation with H, Si, and C are possible, including Sc,H,Si,Si or Sc,H,H,C, but excluding any combination with C in the central position.



Scheme 5. σ-Bond metathesis reactions of silanes at scandocene complexes.

Sadow and Tilley have used the activity of the $[Cp^*_2Sc]$ complexes to catalyze the reaction of methane with diphenylsilane to form Ph_2MeSiH (termed methane dehydrosilation). Five equivalents of Ph_2MeSiH (based on the catalyst concentration) were produced from a solution of $[Cp^*_2ScMe]$ and Ph_2SiH_2 under 150 atm of methane at 80 °C after one week.[22] Dehydrocoupling of silanes to form polysilanes with d^0 metal complexes also proceeds through σ-bond metathesis.[23]

3. The Structure of σ Complexes

3.1. Complexes with a Single σ Ligand

Complexes with a single σ ligand are especially frequent for d^6 metal centers, such as found in $[ML_5]$ (M = Cr, Mo, W) and related $[CpML_2]$ (M = Mn, Re, Fe^+, Ru^+), which are isolobal with BH_3 and have a very low-lying LUMO. We discuss their structures first because they allow comparison between the different families of σ ligands with few complications.

Dihydrogen complexes have been characterized crystallographically for a wide range of metals and several electron configurations.[1,24] The H–H distances determined by neutron diffraction vary from about 0.8 to 1.25 Å, an enormous range. There is an almost complete continuum from complexes with distances close to that of free H_2, through "stretched" dihydrogen complexes, to complete oxidative addition where the H···H separation exceeds 1.8 Å.[25,26] The polyhydride cation $[OsH_5(PMe_2Ph)_3]^+$ exhibits one H···H contact of 1.49(4) Å in the neutron structure that is notably shorter than the other H···H contacts. Careful analysis of this structure suggests that it is a pentahydride rather than a dihydrogen complex and this separation may therefore be described as the shortest H···H contact in a polyhydride complex.[27] Nevertheless, this complex lies on the borderline between dihydrogen complexes and polyhydride complexes.

Complexes with η^2-Si–H bonds have been reviewed by Corey and Braddock-Wilking,[28] by Lin,[29] and also by Nikonov;[30] another very recent review by Lachaize and Sabo-Etienne concentrates on ruthenium silane complexes.[31] Silane complexes formed the first class of σ complexes to be discovered: Hoyano, Elder, and Graham reported the structure of $[Re_2(CO)_8(\mu\text{-}\eta^2,\eta^2\text{-}H_2\text{-}SiPh_2)]$ in 1969.[32] They described the bonding in a way that is indistinguishable from the modern description: "each silicon–hydrogen bond functions as a two-electron donor to rhenium, effectively taking the place of a carbonyl group; the interaction could be described as a three-center two-electron bond with the two electrons supplied by the original Si–H bond".[32] There are numerous examples with X-ray crystal structures. The neutron structure obtained for $[(\eta^5\text{-}C_5H_4Me)Mn(\eta^2\text{-}HSiFPh_2)(CO)_2]$ gives a Si–H bond length of 1.802(5) Å.[33] Silicon–hydrogen distances in the range of 1.7 to 1.9 Å (as measured by X-ray crystallography) are normally assigned as σ-silane coordination whereas higher values, up to 2.4 Å, indicate secondary interactions between a silicon atom and an adjacent hydride (see Section 3.2).[31] The $[Mo(CO)(\text{diphosphine})_2]$ complexes of H_2 and $SiHR_3$ allow one of the best comparisons of $M(\eta^2\text{-}Si\text{-}H)$ and $M(\eta^2\text{-}H\text{-}H)$ bonding. The neutron structure of $[Mo(CO)\{(C_6D_5)_2PCH_2CH_2P(C_6D_5)_2\}_2(\eta^2\text{-}H\text{-}H)]$ shows an H–H distance of 0.736(10) Å with the dihydrogen ligand *trans* to CO.[34] This structure may be compared to the X-ray structure of $[Mo(CO)(Et_2PCH_2CH_2PEt_2)_2(\eta^2\text{-}H\text{-}SiPhH_2)]$ with a silane ligand with a Si–H distance of 1.77(6) Å, although here the σ ligand is *cis* to the carbonyl ligand.[35]

When considering metal–borane complexes, we define σ-borane complexes as containing neutral HBR_2 (or $HB(OR)_2$) ligands that act as two-electron donors. Derivatives with anionic $H_2BR_2^-$, BH_4^- and related ligands that can act as one-electron or three-electron donors and adducts of BH_3 pose different problems and will not be examined. Two recent structures from the very limited class of HBR_2 complexes with $M(\eta^2\text{-}B\text{-}H)$ bonds are illustrated in Figure 3. All the σ-borane manganese complexes of general formula $[(\eta^5\text{-}C_5H_4Me)Mn(CO)_2(\eta^2\text{-}H\text{-}BR_2)]$ reported by Schlecht and Hartwig display a lateral configuration in a four-legged piano-stool geometry.[36] The σ-borane bond is characterized by a B–H length between 1.24(2) and 1.31(2) Å and a $^1J_{B,H}$ coupling constant of 95 Hz. A recent structure shows an η^2-$HBEt_2$ group coordinated to a {Ni(dcpe)} fragment (dcpe = bis(dicyclohexylphosphanyl)ethane) with a B–H bond length of 1.23(5) Å.[37] The complex $[RuH(\mu\text{-}H_2Bpin)(\eta^2\text{-}HBpin)(PCy_3)_2]$ reported by Sabo-Etienne et al. is a unique example allowing a direct comparison between dihydroborate and σ-borane coordination (Figure 3).[38] The σ-B–H bond length (1.35(3) Å) is shorter than the B–H bonds of the dihydroborate ligand (1.58(3) Å and 1.47(3) Å). As in Hartwig's case, the most convincing criterion for σ coordination is the orientation of the BR_2 group.

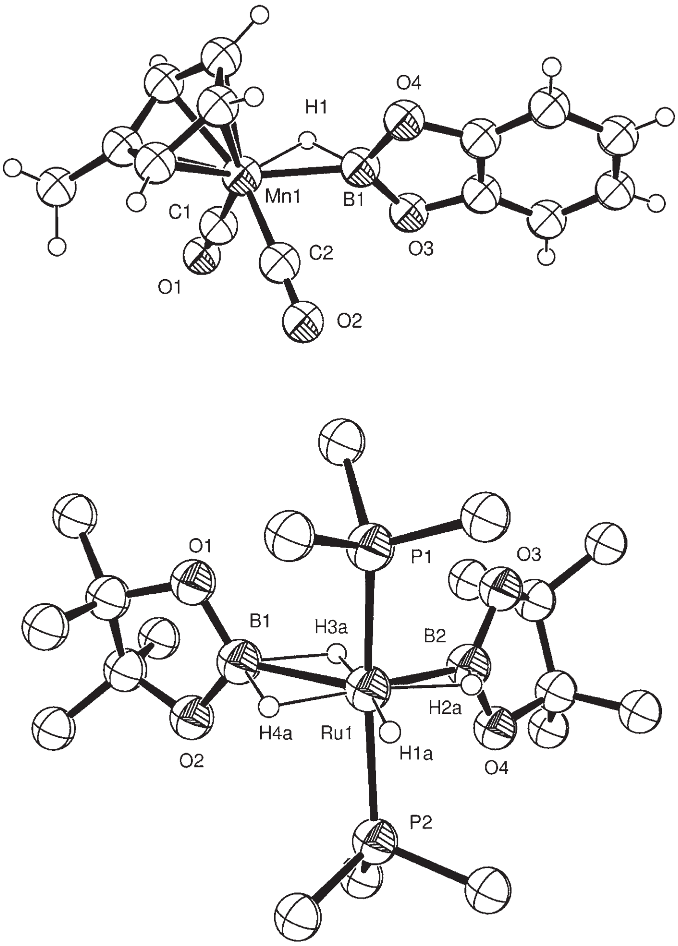
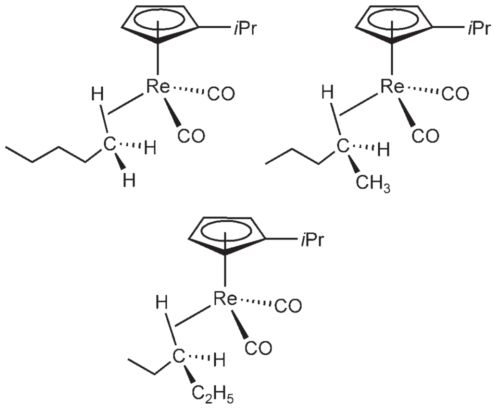


Figure 3. Molecular structures of $[(\eta^5\text{-}C_5H_4Me)Mn(CO)_2(\eta^2\text{-}H\text{-}BO_2C_6H_4)]$ (top)[36] and $[RuH(\mu\text{-}H_2Bpin)(\eta^2\text{-}HBpin)(PCy_3)_2]$ (bottom; HBpin = pinacolborane; the H atoms bound to carbon are omitted and only the C_α atoms of the phosphine ligands are shown).[38]

Complexes of alkanes were reviewed by Hall and Perutz in 1996.[4] Since then, the experimental and theoretical evidence for their existence has become even more compelling.[11–13,39,40] Lersch and Tilset provide an up-to-date and critical assessment of their role in the context of platinum chemistry. They wrote in 2005: "Paradoxically, the alkane C–H σ complexes of Pt [that] have been so firmly entrenched in our mechanistic thinking, have never been directly observed ...".[13] Direct NMR evidence for the structures of alkane σ complexes was lacking until Ball and co-workers reported low-temperature spectra of CpRe derivatives. A major advance was made recently when he obtained NMR spectra of labelled pentane complexes of $\{(\eta^5\text{-}C_5H_4i\text{Pr})Re(CO)_2\}$ with a slight preference for binding of methylene sites (Scheme 6).[5] The structure appears to be very close to those of the corresponding $Mn(\eta^2\text{-}Si\text{-}H)$ and



Scheme 6. σ-Alkane complexes of $\{(\eta^5\text{-}C_5H_4iPr)Re(CO)_2\}$.

$Mn(\eta^2\text{-B-H})$ complexes characterized both by NMR and X-ray diffraction. In 2006, Ball and co-workers reported the NMR spectra of $[CpRe(CO)_2(\eta^2\text{-cyclohexane})]$ and showed that there is a preference for coordination of an axial C–H bond.[41] There are some crystallographically characterized complexes that contain metal σ-alkane bonds although the metal centers are very atypical. In [Fe(double-A-frame porphyrin)(σ-heptane)], disorder prevents clear identification of the structure.[6] However, the η^2-C–H coordination is very clearly established in a group of uranium complexes $[U^{III}\{(OAr)_3\text{triazacyclononane}\}(\sigma\text{-alkane})]$ (alkane = methylcyclohexane, methylcyclopentane, or 2,2,-dimethylbutane); the U–C and U–H distances are about 3.8 and 3.2 Å, respectively.[7]

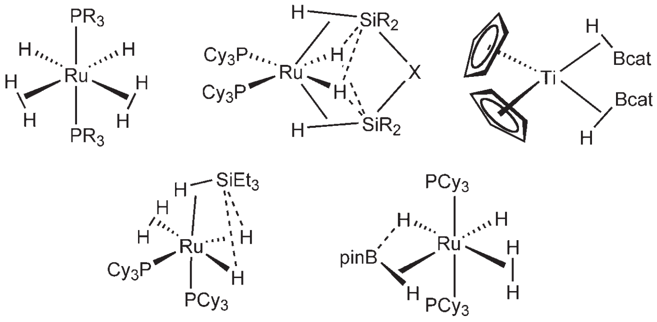
In complexes of the type $[M(\eta^2\text{-E-H})H_n]$ with σ ligands and additional hydride ligands, there is the potential for secondary E···H interactions in which the E···H separation is considerably less than the sum of the van der Waals radii. Such a secondary interaction was first pointed out to explain the surprising orientation of dihydrogen in $[FeH_2(H_2)(PEtPh_2)_3]$ and was designated as a "*cis* interaction".[42,128] It was described as a nascent bond between a hydride and the nearest hydrogen center of the coordinated H_2 ligand. Similar interactions play a major role in silane activation by ruthenium complexes.[31] This point, which is crucial for the purpose of our Review, will be described in more detail in the next section concerning bis(silane) complexes. In monosilane chemistry, the chlorosilane complex $[RuH(\eta^2\text{-HSiMe}_2Cl)\{(\eta^3\text{-}C_6H_8)PCy_2\}(PCy_3)]$ is the best representative example.[43] A 1D HMQC ^{29}Si-^{1}H{^{31}P} experiment shows two doublets in the high-field region with $J_{\mathrm{Si,H}}$ values of 37.3 and 24.1 Hz assigned to the σ-H–Si and the hydride ligands, respectively. The σ-H–Si bond length is 1.91(2) Å by X-ray diffraction (1.891 Å by DFT/B3LYP calculations) whereas the secondary interaction between the hydride ligand and the silicon atom is characterized by a separation of 1.99(2) Å by X-ray diffraction (2.076 Å by DFT/B3LYP calculations).[31] These separations are just on the borderline between primary and secondary Si–H interactions.

Hartwig and co-workers recently isolated the half-sandwich complexes $[Cp^*RhH_2(Bpin)_2]$ and $[Cp^*RhH_2(Bpin)(SiR_3)]$, which appear to involve Rh^V. Close examination of the X-ray structures in conjunction with DFT calculations indicates that they each contain one (η^2-H-Bpin) ligand with additional H···B interactions, so the oxidation state is best formulated as Rh^{III}.[44] In contrast, $[Cp^*Rh(H)_2(SiMe_3)_2]$ shows a genuine Rh^V structure with transoid hydride ligands. The hydride ligands are symmetrically disposed, resulting in equal Si···H separations of 2.27(6) Å.[45] The related complex $[Cp^*Rh(H)(Bpin)_3]$ shows a similar structure with the hydride ligand lying closer to one neighboring boron atom than the other.

The Tp ruthenium complex $[TpRuH(PPh_3)(CH_3CN)]$ catalyzes H/D exchange between CH_4 and deuterated solvents via successive postulated σ-C–H complexes whereas the corresponding dihydrogen and silane complexes, $[TpRuH(\eta^2\text{-E-H})(PPh_3)]$, are isolable and display fast exchange between the hydride and the σ ligand (Tp = hydridotris(pyrazolyl)borate).[46,47]

3.2. Structures with Two σ Ligands

Five types of structures with two σ ligands are known: $M(\eta^2\text{-H-H})_2$, $M(\eta^2\text{-Si-H})_2$, $M(\eta^2\text{-B-H})_2$, $M(\eta^2\text{-Si-H})(\eta^2\text{-H-H})$, and $M(\eta^2\text{-B-H})(\eta^2\text{-H-H})$. We concentrate our discussion on those complexes for which X-ray or neutron data are available; the majority of these complexes include the metal fragment $\{Ru(H)_2(PR_3)_2\}$ (Scheme 7) with the consequence that additional secondary E···H interactions involving the hydride ligands may be present.



Scheme 7. Complexes with two σ ligands; H_2cat = catechol.

The neutron diffraction structure of $[Ru(H)_2(\eta^2\text{-H-H})_2(PCyp_3)_2]$ (Cyp = cyclopentyl) shows two bonded H–H ligands with distances of 0.825(8) Å and 0.835(8) Å while the nonbonded distances are close to 2.1 Å, indicating the absence of secondary H···H interactions.[48]

In contrast, the X-ray structure of $[Ru(H)_2\{(\eta^2\text{-H-SiMe}_2)CH_2CH_2(\eta^2\text{-H-SiMe}_2)\}(PCy_3)_2]$ shows two η^2-Si–H bonds of approximate length 1.75 Å and four secondary H···Si interactions of about 2.2 Å each (compare the sum of the van der Waals radii: 3.4 Å).[49] The presence of the secondary interactions is confirmed by DFT calculations. The same features are found for several complexes with different phosphines and different disilanes. The secondary interactions are maximized with the *cis* geometry of the phosphines, an unusual arrangement for such bulky ligands.[31]

The combination of one dihydrogen ligand and one η^2-Si–H ligand is illustrated by $[Ru(H)_2(\eta^2\text{-H-SiPh}_3)(\eta^2\text{-H}_2)$-

$(PCy_3)_2$]. Once more, the phosphine ligands adopt a *cis* geometry and secondary interactions are present, characterized by Si···H separations of around 2.1 Å.[50]

There is one example of an analogous complex, $[Ru(H)_2(\eta^2\text{-H-H})(\eta^2\text{-H-Bpin})(PCy_3)_2]$ with the η^2-Si−H ligand replaced by an η^2-B−H ligand, but its geometry is significantly different.[51] The phosphine ligands now adopt a *trans* arrangement, and the dihydrogen ligand lies parallel to the P-Ru-P axis to avoid competition with the σ-borane ligand. The coordination mode of the borane ligand is clearly of a σ-borane type as attested by a B−H bond length of 1.30(2) Å (1.362 Å by DFT/B3LYP), whereas the interaction between the other hydride ligand and the boron atom is shown to be much weaker (separation: 1.89(2) Å; 2.003 Å by DFT/B3LYP).[51]

The only example of a complex with two η^2-B−H ligands was, in fact, the first σ-borane complex to be characterized. Hartwig, Eisenstein, et al. identified the σ-borane coordination of $[Cp_2Ti^{II}(HBcat)_2]$ in 1996 on the basis of NMR spectroscopy, X-ray diffraction, and MP2 calculations.[52,53]

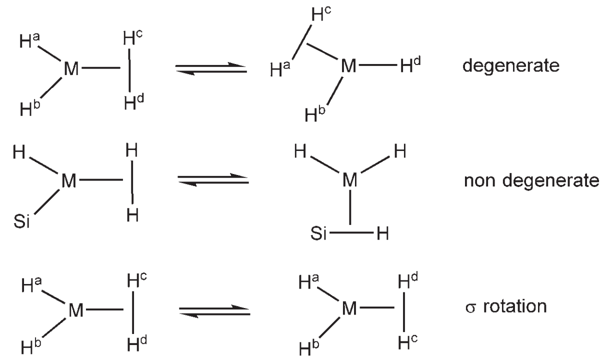
There are indeed no examples of structures incorporating a $M(\eta^2\text{-C-H})_2$ fragment, but it is interesting to mention some related agostic structures. The cationic iridium complex $[Ir(H)_2(PtBu_2Ph)_2]^+$ was formulated as having two agostic interactions through X-ray diffraction (the hydride ligands and the agostic C−H unit were not located), IR and NMR spectroscopy, and computational studies.[54] Further structures with two agostic interactions without additional hydride ligands have been reported for $[RuCl_2\{PPh_2(2,6\text{-}Me_2C_6H_3)\}_2]$,[55] $[Mn(CO)(dppe)_2]^+$ (dppe = $Ph_2PCH_2CH_2PPh_2$),[56] and $[RuPh(CO)(PtBu_2Me)_2]^+$.[57] The ruthenium complex $[RuH(H_2)(2\text{-}PhC_5H_4N)(PiPr_3)_2]^+$ incorporates dihydrogen, hydride, and agostic ligands.[58]

4. Dynamics of σ Complexes

Dynamic exchange phenomena are observed in most complexes with hydride and σ-E−H ligands. The processes exchange the different types of hydrogen atom; they may be degenerate or may make species with new σ-E−H bonds that act as intermediates. Even in complexes with no σ-E−H bonds in the ground state, dynamic exchange may occur through σ-E−H intermediates or transition states. Wherever there is a σ-E−H ligand, there is the possibility of σ rotation, that is, rotation about the M−EH bond, if the process is truly intramolecular (Scheme 8).[1] In the succeeding section, we will show that the dynamic behavior has an important bearing on the reactivity.

4.1. $[MH_x(\eta^2\text{-H-H})_y]$ (x, y ≠ 0)

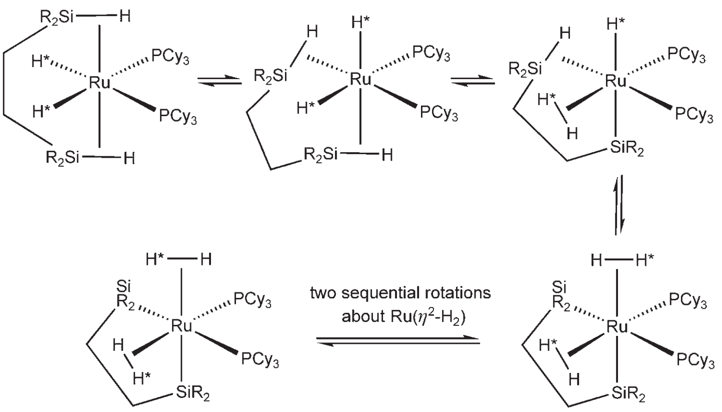
Dynamic exchange phenomena among complexes of the class $[MH_x(\eta^2\text{-H-H})_y]$ are usually so fast that a single hydride resonance is observed in the ^{1}H NMR spectrum at all accessible temperatures. In consequence, it is often very challenging to prove the existence of the metal–dihydrogen bond. An early exception was $[ReH_2(\eta^2\text{-H}_2)(CO)(PMe_2Ph)_3]^+$ in which the H_2 ligand and the two hydride ligands are distinguished in the low-temperature ^{1}H NMR spectrum.[59] Moreover, the tetrahydride isomer is also present at equilibrium. On warming, the dihydrogen ligands and the hydride ligands of $[ReH_2(\eta^2\text{-H}_2)(CO)(PMe_2Ph)_3]^+$ exchange well below the onset temperature for exchange with the tetrahydride isomer. This observation led Luo and Crabtree to postulate that exchange of the dihydrogen and hydride ligands occurs via a trihydrogen intermediate or transition state and not via the tetrahydride complex. At about the same time, Eisenstein, Caulton, et al. suggested that the attractive secondary interaction ("*cis* effect") between the hydride and dihydrogen ligands of $[Fe(H)_2(\eta^2\text{-H}_2)(PEtPh_2)_3]$ acted as a preliminary step toward scrambling of the hydrogen atoms without the necessity of passing through a classical tetrahydride intermediate.[128] The complexes $[Ru(H)_2(\eta^2\text{-H-H})_2(PR_3)_2]$ (R = *i*Pr, Cy, Cyp) show no decoalescence down to 173 K.[48,60] Unusually, decoalescence is observed in $[Ru(H)_2(\eta^2\text{-H-H})(L)(L')_2]$ when L is very different from L′ (L = CO, L′ = P*i*Pr$_3$;[61] L = 2-phenyl-3,4-dimethylphosphaferrocene, L′ = PCy$_3$;[62] LL′$_2$ = $PhP(CH_2CH_2CH_2PCy_2)_2$).[63] The *ansa* metallocene cation $[\{(\eta^5\text{-}C_5H_4)_2CMe_2\}Mo(H)(\eta^2\text{-H}_2)]^+$ provides a further example with thorough analysis and decoalescence of isotopomers when partially deuterated.[64] The orthometalated phenylpyridine species $[RuH(\eta^2\text{-H-H})(ph\text{-}py)(PiPr_3)_2]$ (ph-py = 2-$C_6H_4C_5H_4N$) is a rare case in which quantum exchange between a hydride and a σ-dihydrogen ligand can be established unequivocally by NMR spectroscopy (see Section 5.1).[65]



Scheme 8. Dynamic rearrangements of metal hydrido dihydrogen complexes.

4.2. $[MH_x(\eta^2\text{-H-Si})_y]$ and $[MH_x(\eta^2\text{-H}_2)(\eta^2\text{-H-Si})]$ (x, y ≠ 0)

The ^{1}H NMR spectrum of $[Ru(H)_2\{(\eta^2\text{-H-SiMe}_2)CH_2CH_2(\eta^2\text{-H-SiMe}_2)\}(PCy_3)_2]$ displays one signal each at room temperature for the two (η^2-H-Si) units and the two classical hydride ligands. Coalescence occurs at 376 K with $\Delta H^{\ddagger} = (77 \pm 11)\,\mathrm{kJ\,mol^{-1}}$ and $\Delta S^{\ddagger} = (14 \pm 34)\,\mathrm{J\,K^{-1}\,mol^{-1}}$. The exchange pathway was demonstrated by DFT calculations to involve three isomers.[66] The initial step is an isomerization to a species with *cis* η^2-H−SiMe$_2$ groups. In the second stage, an isomer is formed with one dihydrogen ligand, one η^2-H−SiMe$_2$ ligand, and a classical silyl group; this isomer is followed by a third isomer with two dihydrogen ligands and two classical silyl groups. Reversal of this sequence allows complete exchange of the hydrogen atoms (Scheme 9). The transition state of the first step corresponds to the highest barrier of the exchange process and is characterized by the breaking of the secondary Si···H interactions.[66] The mechanism is similar for the complex with a C_6H_4 bridge between the silyl groups, but the geometries are constrained differently with a short bridge. For the complexes $[Ru(H)_2\{(\eta^2\text{-}H\text{-}SiMe_2)X(\eta^2\text{-}H\text{-}SiMe_2)\}(PCy_3)_2]$ (with X = O, NH) the barriers are much lower and two stages of decoalescence are observed at much lower temperatures leading to inequivalence of all four hydrogen atoms.[66,67] Nevertheless, the principles of the mechanism are the same.



Scheme 9. Mechanism of hydrogen exchange for $[Ru(H)_2\{(\eta^2\text{-}H\text{-}SiMe_2)CH_2CH_2(\eta^2\text{-}H\text{-}SiMe_2)\}(PCy_3)_2]$.

In the series of Tp(monosilane) complexes $[TpRuH(\eta^2\text{-}H\text{-}SiR_3)(PPh_3)]$, the hydride ligands remain equivalent down to 173 K.[47] In the Cp*Rh monosilane complex $[Cp^*RhH(\eta^2\text{-}H\text{-}SiPh_3)(PMe_3)]^+$, only one hydride resonance is observed at room temperature.[68] In the monosilane dihydrogen complex $[Ru(H)_2(\eta^2\text{-}H_2)(\eta^2\text{-}H\text{-}SiPh_3)(PR_3)_2]$, no decoalescence was observed even at very low temperature.[50] In contrast, the two hydride ligands in $[Ru(H)(H\text{-}SiMe_2Cl)[P(\eta^3\text{-}C_6H_9)Cy_2](PCy_3)]$ are inequivalent as a result of the presence of two different phosphine ligands, and display two different $J_{Si,H}$ coupling constants (37 and 24 Hz).[43]

4.3. $[MH_x(\eta^2\text{-}H\text{-}B)_y]$ (x = 0, y = 2; x = 1, y = 1), $MH_2(\eta^2\text{-}H_2)(\eta^2\text{-}H\text{-}B)$, and $M(\eta^2\text{-}H\text{-}B)(\eta^2\text{-}H\text{-}Si)$

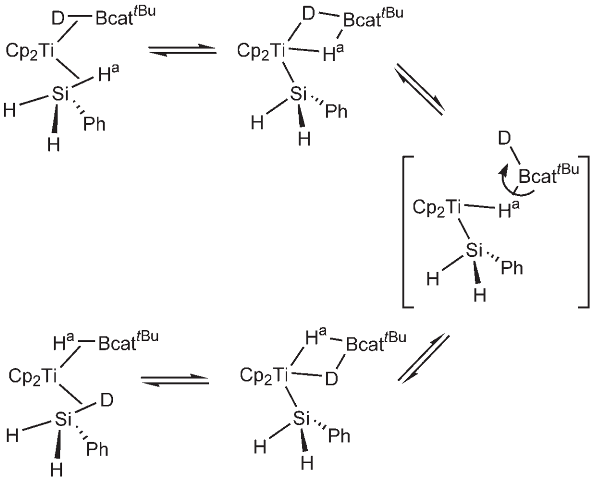
As for the monosilane dihydrogen complex, fast exchange on the NMR timescale is observed in the borane dihydrogen complex $[Ru(H)_2(\eta^2\text{-}H_2)(\eta^2\text{-}H\text{-}Bpin)(PCy_3)_2]$ down to 183 K. Three hydride signals are observed below 253 K for the borane complex $[RuH(\mu\text{-}H_2Bpin)(\eta^2\text{-}H\text{-}Bpin)(PCy_3)_2]$, whereas it is very difficult to see any signal at room temperature. All the hydride ligands are probably exchanging above room temperature but no coalescence signal could be detected.[38,51]

The first σ-borane complex, which was isolated in 1996, is a titanocene complex incorporating two σ-catecholborane ligands.[52] Its reaction with H_3SiPh leads to the formation of the (σ-borane)(σ-silane) complex $[Cp_2Ti(\eta^2\text{-}H\text{-}Bcat)(\eta^2\text{-}H\text{-}SiH_2Ph)]$, which shows two hydride resonances. Exchange of the two hydride ligands is demonstrated by deuteration at 243 K.[53] Scheme 10 shows the proposed mechanism, which involves a dihydroborate intermediate.

$[Cp^*RhH_2(Bpin)(SiEt_3)]$ shows a single hydride resonance although the structural evidence indicates a closer H···B than H···Si contact.[44]

5. Dynamics of Hydride Complexes Implicating σ Complexes as Postulated Intermediates

Hydride complexes incorporating either another hydride ligand or a silyl or an alkyl group are capable of rearrangement processes involving σ complexes as postulated reaction intermediates (and not just transition states). We will illustrate this type of reaction rather than doing a comprehensive survey.



Scheme 10. Mechanism of hydrogen exchange of $[Cp_2Ti(\eta^2\text{-}H\text{-}Bcat)(\eta^2\text{-}H\text{-}SiH_2Ph)]$.

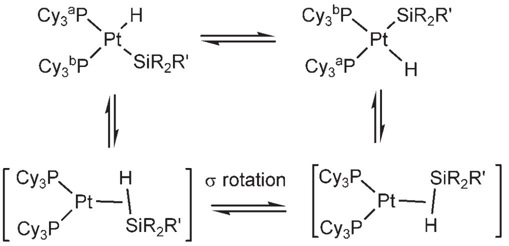
5.1. $M(H)_x$ via $M(H)_{x-2}(\eta^2\text{-}H\text{-}H)$ Quantum Tunneling

The phenomenon of quantum tunneling is now well-established in trihydride complexes. One of the mechanisms proposed by Limbach and co-workers involves a pre-equilibrium with a hydride–dihydrogen complex in which quantum exchange occurs between the two nuclei of the dihydrogen ligand.[42,69,70] Strong evidence to support this theory comes from the $[Cp_2TaH_2L]^+$ series of complexes, examples of which can be isolated with dihydride or dihydrogen structures according to the choice of L. The complex with L = CO was identified as a dihydrogen complex both by X-ray diffraction and NMR spectroscopic data while the species with L =

phosphite was characterized as a dihydride complex. Exchange couplings varied from 76 Hz to 12 Hz for L = P(OMe)$_3$ whereas a value greater than 3200 Hz was estimated for L = CO.[71]

5.2. MH(SiR$_3$) via M(η^2-H-SiR$_3$)

Monohydride silyl complexes display exchange processes that are revealed by coupling to other nuclei. An early example[72] was *cis*-[PtH(SiPh$_3$)(PCy$_3$)$_2$] which was revisited recently[73] using a series of silanes. Intramolecular exchange averages the phosphorus environments without generating the *trans* isomer. Exchange is postulated to occur through a [Pt(η^2-H-SiR$_3$)] intermediate (Scheme 11).



Scheme 11. Mechanism of phosphorus exchange of *cis*-[PtH(SiR$_2$R')(PCy$_3$)$_2$] via σ-silane intermediate.

Complexes of the type [CpRhH(SiR$_3$)(C$_2$H$_4$)] are chiral at the rhodium center, but exchange between enantiomers cannot be detected by NMR spectroscopy. Such exchange can, however, be revealed when the ethylene ligand is replaced by H$_2$C=CHCO$_2$*t*Bu. The spectra of [CpRhH(SiR$_3$)(H$_2$C=CHCO$_2$*t*Bu)] show two isomers characterized by two hydride resonances that undergo mutual exchange. For the triethylsilyl complex (R = Et), the two hydride resonances broaden at the same rate as the temperature is increased, whereas for the trimethoxysilyl complex (R = OMe), broadening occurs at different rates. The observations for the triethylsilyl complex are consistent with a [Rh(η^2-H-SiR$_3$)] species either as an intermediate or as a transition state. In contrast, for the trimethoxysilyl complex, a [Rh(η^2-H-SiR$_3$)] intermediate is required to satisfy the observation and a transition state alone is insufficient.[74]

In [CpRhH(SiMe$_3$)$_3$] all the silyl ligands remain equivalent by NMR spectroscopy down to 197 K, implicating exchange of SiMe$_3$ ligands since the molecule should adopt a four-legged piano-stool structure. The $J_{\mathrm{Si,H}}$ value of 13.5 Hz is consistent with a rhodium(V) structure. With inequivalent silyl groups as in [CpRhH(SiEt$_3$)(SiMe$_3$)$_2$], two $J_{\mathrm{Si,H}}$ values (24 and 6 Hz) are obtained at room temperature in agreement with the intermediacy of a [Rh(η^2-H-SiR$_3$)] structure to explain the exchange process.[75]

5.3. MH(CH$_2$R) via M(η^2-H-CH$_2$R)

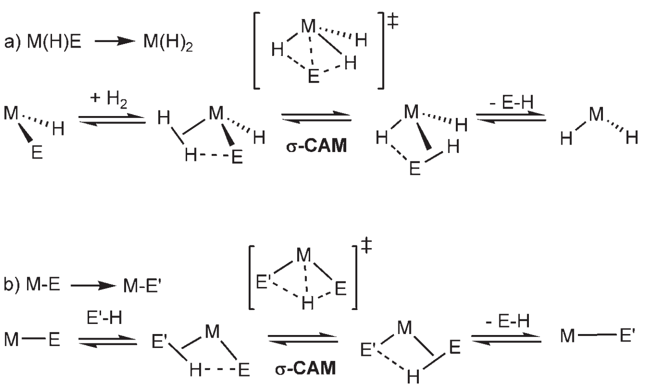
Metal alkyl hydride complexes often exhibit degenerate exchange between the hydride ligand and the α-hydrogen atoms of the alkyl group that is revealed by selective deuteration, line broadening, kinetic isotope effects, or equilibrium isotope effects.[11] The accepted mechanism of exchange involves a M(η^2-H-C) intermediate, a principle that receives strong support from theory. Early examples are summarized by Crabtree, Hall, and Perutz as well as by Shilov and Shul'pin.[3,4,14] The exchange of methyl and hydride protons in [Cp*OsH(Me)(dmpm)]$^+$ (dmpm = bis(dimethylphosphanyl)methane) is manifested by line broadening and spin-saturation transfer. An Os(η^2-CH$_4$) intermediate is accessed with $\Delta H^{\neq} = (30 \pm 4)\,\mathrm{kJ\,mol^{-1}}$ and $\Delta S^{\neq} = (-27 \pm 21)\,\mathrm{J\,K^{-1}\,mol^{-1}}$.[76] An example from the very extensive studies on platinum complexes is the reaction of [Pt(diimine)(CH$_3$)$_2$] (diimine = ArN=CMe-CMe=NAr; Ar = 3,5-(CF$_3$)$_2$C$_6$H$_3$) with DOTf, which yields a mixture of CH$_3$D and CH$_4$. The intermediacy of σ-methane complexes allows equilibration between the [Pt(D)(CH$_3$)$_2$]$^+$ and the [Pt(H)(CH$_2$D)(CH$_3$)]$^+$ derivatives.[77] Similar alkane intermediates have been postulated in the formation and exchange reactions of a wide range of alkyl hydride complexes such as [RhH(CH$_2$R)(tacn) L]$^+$ (tacn = triazacyclononane),[78] [Tp*RhH(CH$_2$R) L] (Tp* = tris(3,5-dimethylpyrazolyl)borate),[12,79] [{H$_2$Si(C$_5$H$_4$)$_2$}WH(Me)],[80] [Tp*PtH(Me)$_2$],[81] and related platinum complexes.[13,40]

Two classes of Pt-catalyzed alkane-activation reactions have received particular attention. The Shilov system involves Pt$^{\mathrm{II}}$ salts as catalysts in aqueous acidic media with Pt$^{\mathrm{IV}}$ salts as oxidants.[14,82] The Catalytica system employs [Pt(bipyrimidine)Cl$_2$] as catalyst in fuming sulfuric acid with sulfur trioxide as oxidant.[83,84] Both systems exhibit multiple H/D exchange reactions of methane and other simple alkanes under appropriate conditions, thus implying the existence of dynamic exchange with bound methane. Indeed, the evidence for exchange via Pt-bound alkanes goes back to 1968.[85] Theoretical studies have addressed the question of whether the reactions proceed by oxidative addition or whether Pt$^{\mathrm{II}}$ alkyl compounds are formed at constant oxidation state. The latter reactions are often described as electrophilic substitutions at the alkane, but may also be described as σ-bond metathesis processes with loss of H$^+$. The mechanistic questions are particularly challenging to address by theory because of the acidic media. The reader is referred to the critical assessment in a review article by Lersch and Tilset.[13]

6. σ-CAM Mechanisms

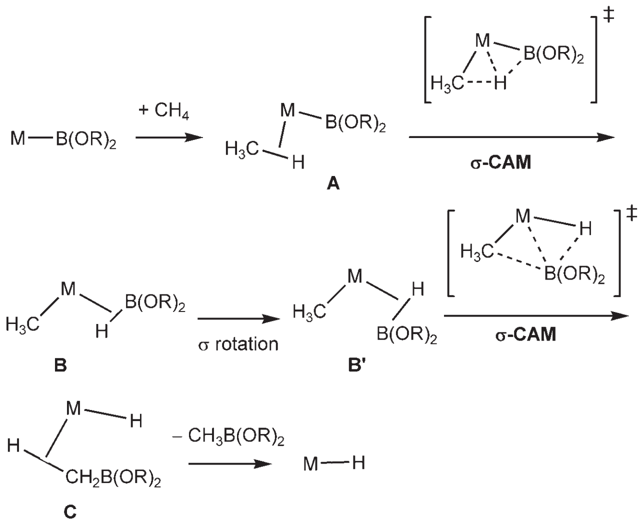
Metathesis mechanisms are typically drawn with a single four-center transition state and no intermediates (see Scheme 3). As early as 1990, Luo and Crabtree found evidence that exchange between dihydrogen and hydride ligands in a {Re(η^2-H$_2$)(H)$_2$} complex occurred via a trihydrogen transition state or intermediate and not by an oxidative addition pathway that would have led to a tetrahydride intermediate.[59] In 1993, Crabtree pointed out the role of σ complexes as likely precursors to general four-center transition states in sigma-bond metathesis reactions on the basis of the fluxional processes observed in dihydrogen complexes.[3] In 2002, several findings on dihydrogen and silane ruthenium systems led us to propose that a general σ-bond metathesis mechanism could be drawn starting at a conventional d^6 MH(E) complex by reaction with H_2 to form a dihydrogen complex, conversion of σ-H–H to σ-E–H, and return to d^6 $M(H)_2$ by elimination of EH (Scheme 12a).[66] This type of mechanism may also be extended by starting at M–E (Scheme 12b). Since 2002, the mechanism has also been proposed for several other specific reactions, and we name this pathway a σ-complex-assisted metathesis (σ-CAM) mechanism.

σ-CAM mechanisms involve discrete σ complexes as intermediates and exploit the abilities of σ complexes to undergo dynamic rearrangements that we have demonstrated in Sections 4 and 5. These two features set them apart from traditional σ-bond metathesis mechanisms. Both σ-CAM mechanisms and the traditional oxidative addition and reductive elimination processes of Scheme 2 involve σ complexes, but they differ in the oxidation state changes. σ-CAM mechanisms operate at constant oxidation state whereas in oxidative addition and reductive elimination mechanisms the metal center changes oxidation states by two units. Such mechanisms could operate during several catalytic processes involving, in particular, dihydrogen, silane, borane, and alkane activation. Scheme 12 shows the multicenter transition states for the σ-CAM step; calculations show that there is another alternative for the transition state in which the links between the nonmetal atoms are broken.[46] This type of transition state has been described as corresponding to oxidative addition; however, we avoid this description because of the risk of confusion.



Scheme 12. σ-Complex-assisted metathesis.

In 2003 Hartwig proposed a pathway for alkane borylation at $[CpM(CO)_n(\text{boryl})]$ complexes (M = Fe, W) on the basis of DFT calculations (Scheme 13).[86] It involves a σ-CAM step converting σ-alkane **A** to σ-borane **B** as in Scheme 12 together with a second σ-CAM step converting σ-borane **B′** after σ rotation to a σ-alkylborane **C** with B–C bond coupling. The calculations suggest conversion directly from **B′** to **C** through a multicenter transition state without the intermediacy of a σ-B–C complex. More recently, Hartwig et al. have extended this mechanism to start at $[CpRhH\{B(OR)_2\}]$ or $[CpRh\{B(OR)_2\}_2]$, but with very similar principles.[87]



Scheme 13. Mechanism of methane borylation with σ-CAM steps.

At a similar time to Hartwig's publication, Ng et al. recognized that the dynamic exchange of hydrogen in the complexes $[TpRu(H)(\eta^2\text{-E-H})(PPh_3)]$ (E = H, SiR_3) implied that it was possible to interconvert σ complexes without oxidative addition.[46] They demonstrated that $[TpRu(H)(MeCN)(PPh_3)]$ catalyzes H/D exchange between methane and C_6D_6 at 100 °C. Similar catalytic exchange is observed with H_2 instead of CH_4. The authors proposed mechanisms of exchange, shown in simplified form in Equations (3) and (4) for hydrogen and methane, respectively, on the basis of DFT calculations.

$$\begin{aligned}&[\{Ru\}H(\eta^2\text{-}H_2)] + C_6D_6 \rightarrow [\{Ru\}H(\eta^2\text{-}C_6D_6)]\\&\rightarrow [\{Ru\}(C_6D_5)(\eta^2\text{-H-D})], \text{ etc.}\end{aligned}\tag{3}$$

$$\begin{aligned}&[\{Ru\}H(\eta^2\text{-}C_6D_6)] \rightarrow [\{Ru\}(C_6D_5)(\eta^2\text{-HD})]\\&\rightarrow [\{Ru\}D(\eta^2\text{-}C_6D_5H)] \xrightarrow{CH_4} [\{Ru\}D(\eta^2\text{-H-}CH_3)] + C_6D_5H\\&\rightarrow [\{Ru\}(CH_3)(\eta^2\text{-H-D})] \rightarrow [\{Ru\}H(\eta^2\text{-D-}CH_3)], \text{ etc.}\end{aligned}\tag{4}$$

These mechanisms rely on σ-CAM and σ-rotation steps involving dihydrogen and methane ligands as well as η^2-benzene complexes. The calculations show that the transition states for the σ-CAM step can break the bonds between the nonmetal atoms bound to the metal center. In a subsequent paper, Lam et al. compare the behavior of Fe, Ru, and Os in the metathesis processes shown in Equation (5) (M = $Fe(Tp)(PH_3)$, $Ru(Tp)(PH_3)$, $Os(Tp)(PH_3)$) via DFT calculations.[88]

$$\begin{aligned}&[MH] + CH_4 \rightarrow [MH(\eta^2\text{-H-}CH_3)]\\&\rightarrow [M(CH_3)(\eta^2\text{-H-H})] \rightarrow [M(CH_3)] + H_2\end{aligned}\tag{5}$$

It was shown that the mechanism conforms exactly to the σ-CAM route of Scheme 12b in the case of Fe and is very close to it in the case of Ru. In contrast, an oxidative cleavage mechanism is followed for M = Os (see Scheme 2c). The degenerate exchange step in the methyl(η^2-methane) analogue is also examined with similar results [Eq. (6); M = Fe(Tp)(PH$_3$), Ru(Tp)(PH$_3$), Os(Tp)(PH$_3$), Pt(H$_2$NCH$_2$CH$_2$NH$_2$)(NF$_2$H)$^+$].

$$[\mathrm{M(CH_3)(\eta^2\text{-}CH_4)}] \rightarrow \text{intermediate from oxidative cleavage or } \sigma\text{-CAM transition state} \rightarrow [\mathrm{M(\eta^2\text{-}CH_4)(CH_3)}] \qquad (6)$$

There is a significant difference between metals in the transition states for the σ-CAM step: iron has a multicenter transition state while the C–H and H–H bonds are completely broken in the transition state for ruthenium. This study may be contrasted with theoretical models of the methane exchange observed on treatment of [Pt(Me$_2$NCH$_2$CH$_2$NMe$_2$)(L)(CH$_3$)]$^+$ (L = pentafluoropyridine) with ^{13}CH$_4$.[89] The degenerate exchange reaction of the [Pt(CH$_3$)(η^2-CH$_4$)]$^+$ cation is shown to have a much lower barrier with an oxidative cleavage mechanism than a σ-bond metathesis mechanism and consequently σ-CAM is excluded.[90]

It is remarkable that, despite the differences between H, Si, B, and C, similar σ complexes and dynamics can occur, as shown in the previous examples. The simplicity of the dihydrogen ligand contrasts with the more complex bonding of the other σ ligands. The hypervalence properties of Si (low-lying σ* orbital) allow for secondary interactions upon silane coordination and the substituents on the silicon atom can tune the energy levels. For boron, the vacant p orbital allows boranes to act as Lewis acidic ligands. This effect is moderated when there are oxygen substituents present through O–B p_π–p_π bonding. Indeed, σ-borane chemistry is dominated by pinacol and catechol boranes. In contrast, alkanes have neither the hypervalency nor the vacant p orbital, and the σ* orbital lies relatively high in energy.

Hydrogenolysis processes form one group of stoichiometric reactions that may proceed by σ-CAM mechanisms. For instance, the reaction of a metal alkyl compound with hydrogen often generates a metal hydride and alkane. Examples of iron boryl complexes that react with H$_2$ to form iron hydrides and borane may proceed similarly.[91,92] A related reaction of [CpFe(BPh$_2$)(CO)$_2$] with HBcat results in boryl exchange, yielding [CpFe(Bcat)(CO)$_2$].[91] These reactions may also proceed by a σ-CAM mechanism. An example of a silylation of a hydride that proceeds via a σ-silane complex is the reaction of [RuD(Cl)(η^2-D$_2$)(PCy$_3$)$_2$] with HSiMe$_2$Cl to form [Ru(SiMe$_2$Cl)(Cl)(η^2-H-D)(PCy$_3$)$_2$].[43] Of course, such steps are closely related to those commonly observed at d^0 centers, such as the reactions leading to polysilane formation.[23]

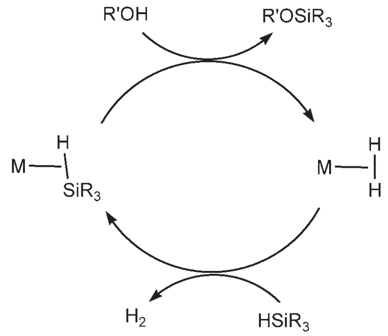
The evidence for σ-CAM mechanisms in C–H activation chemistry of late transition metals is less clear than for hydrogen, silane, and borane activation, but the examples mentioned above provide strong support for it. As pointed out above, σ-C–H coordination lacks the assistance of low-lying empty orbitals. We should search for such mechanisms in reactions where the product and starting material are in the same oxidation state (including isotope exchange processes). At present, there are some examples such as Bergman's C–H activation at Ir^{III} centers where a σ-bond metathesis mechanism has been excluded on the basis of calculations.[93–95] There are other plausible candidates for the σ-CAM mechanism for C–H activation where the mechanism is not clearly established.[96,97]

7. Catalysis Assisted by σ Complexes

7.1. Examples of Dihydrogen and Silane Complexes as Intermediates

The role of dihydrogen complexes as homogeneous reduction catalysts was reviewed in 1998 by Esteruelas and Oro.[98] In 2005, Kubas reviewed examples of catalytic processes involving σ complexes,[99] and assembled evidence for their role both as precursors and as intermediates in catalytic cycles. Here, we pick out a few examples of major relevance to this study. Poliakoff and co-workers provided conclusive evidence for the involvement of dihydrogen complexes in the photocatalytic hydrogenation of dienes (by time-resolved IR spectroscopy and IR spectroscopy in liquified xenon solutions).[100,101] They demonstrated the involvement of [Cr(CO)$_4$(η^4-diene)(η^2-H$_2$)] and showed that discrimination between the norbornene and nortricyclene products that arise from norbornadiene may be traced to the position of the H$_2$ ligand with respect to the diene. The hydrogenation takes place without oxidative addition, and the chromium center remains in oxidation state zero. Subsequent studies with parahydrogen-enhanced NMR spectroscopy supported the mechanism.[102] IR studies in polyethylene matrices of photocatalytic hydrogenation of dimethylfumarate by [Fe(CO)$_4$(η^2-dimethylfumarate)] showed that the same principles extend to this system.[103] In contrast, photocatalytic hydrosilation of dienes by [Cr(CO)$_6$] is thought to involve both σ-silane coordination and subsequent oxidative addition, yielding the 1,4-hydrosilation product via a [Cr(CO)$_3$(η^3-dienyl)(silyl)] species.[104]

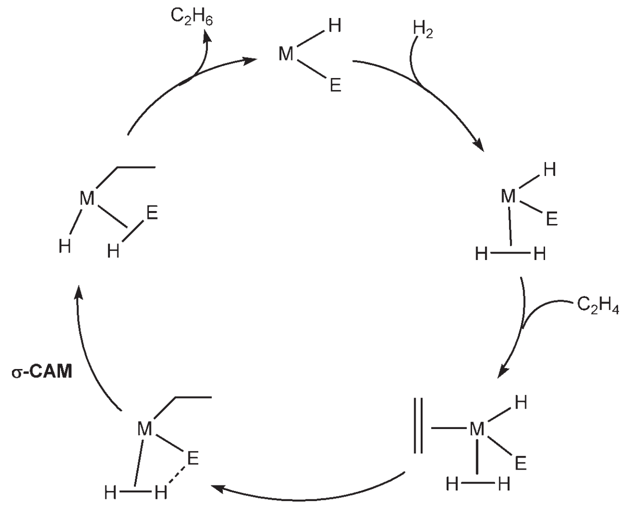
Catalytic silane alcoholysis converts silanes R$_3$SiH into silyl ethers R$_3$SiOR′ by reaction with alcohols R′OH. Dihydrogen and η^2-silane complexes (including bis(η^2-silane) complexes) have been identified as intermediates in cationic iridium, iron, and manganese systems (Scheme 14). The reactions can proceed at constant oxidation state with nucleophilic attack of the alcohol on the coordinated silane.[105–107]



Scheme 14. Mechanism of catalytic silane alcoholysis with [M(η^2-HSiR$_3$)] and [M(η^2-H$_2$)] intermediates.

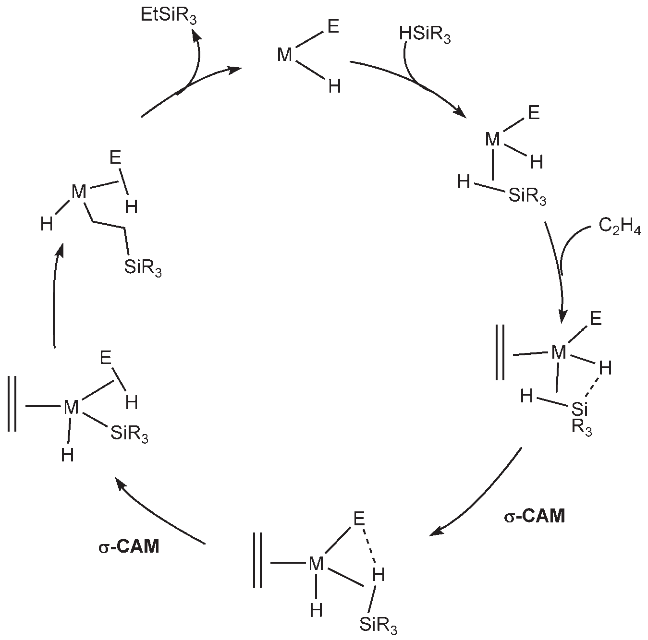
7.2. Catalysis via σ-CAM Mechanisms

It is now possible to formulate cycles for several standard catalytic reactions in organometallic chemistry by employing a σ-CAM sequence. We have already summarized the H/D exchange reactions investigated by Ng et al. in which a sequence of σ-CAM steps interconvert σ-H–H, σ-H–CH_3, and η^2-benzene complexes.[46] This investigation showed that alkane and hydrogen activation at first- and second-row transition metals may proceed catalytically through the σ-CAM route. The authors note that there are several other exchange reactions mentioned in the literature that may proceed similarly. Scheme 15 shows a general alkene hydrogenation pathway starting with an M(E)H fragment involving σ-dihydrogen intermediates. An analogous scheme for hydrosilylation with the intermediacy of σ-silane and σ-dihydrogen species is shown in Scheme 16. The latter shows two σ-CAM steps in succession, but this particular sequence is not unique. These cycles probably apply also when $[Ru(H)_2(\eta^2\text{-H-H})_2(PCy_3)_2]$ is used as a catalyst precursor for hydrogenation or hydrosilylation.



Scheme 15. A catalytic hydrogenation mechanism at constant oxidation state with a σ-CAM step.

Alkane complexes are widely recognized as intermediates in C–H bond activation, though typically it is postulated that formation of an alkane complex is followed by oxidative cleavage. In principle, the hydrogenation cycle could be adapted to alkane dehydrogenation as the microscopic reverse. However, the examples studied in detail usually involve third-row transition metals and are now understood to involve oxidative addition/reductive elimination sequences.[108–110]



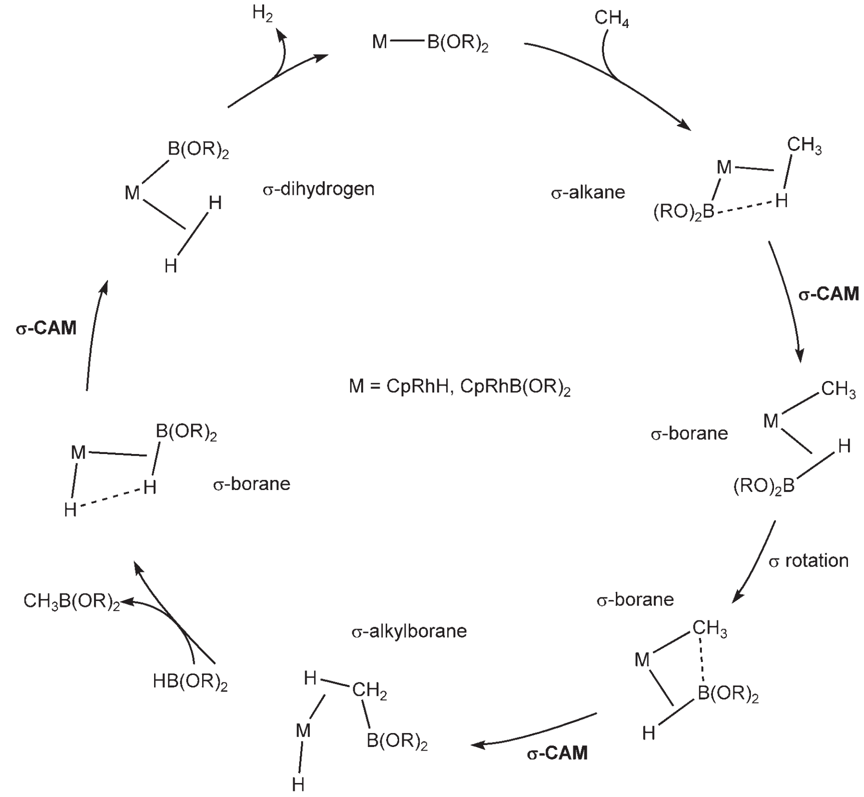
Scheme 16. A catalytic hydrosilylation mechanism at constant oxidation state with σ-CAM steps.

We have drawn a complete cycle for alkane borylation on the basis of the DFT calculations by Hall and Hartwig (Scheme 17). This cycle includes σ-dihydrogen, σ-alkane, and σ-borane intermediates and maintains a constant +3 oxidation state for the Rh center. However, the evidence does not yet make a clear distinction between Rh^{III} and Rh^{V} formulations of $[Cp^*Rh(H)_2\{B(OR)_2\}_2]$.[87] The cycle includes the same type of B–C bond-forming steps as are shown in Scheme 13. The cycle can start at either 16-electron $[CpRhH\{B(OR)_2\}]$ or $[CpRh\{B(OR)_2\}_2]$ (note that the experimental system employs Cp* ligands, whereas the theoretical results are obtained with Cp ligands; the pinacolate substituents on boron were replaced by OCH_2CH_2O).

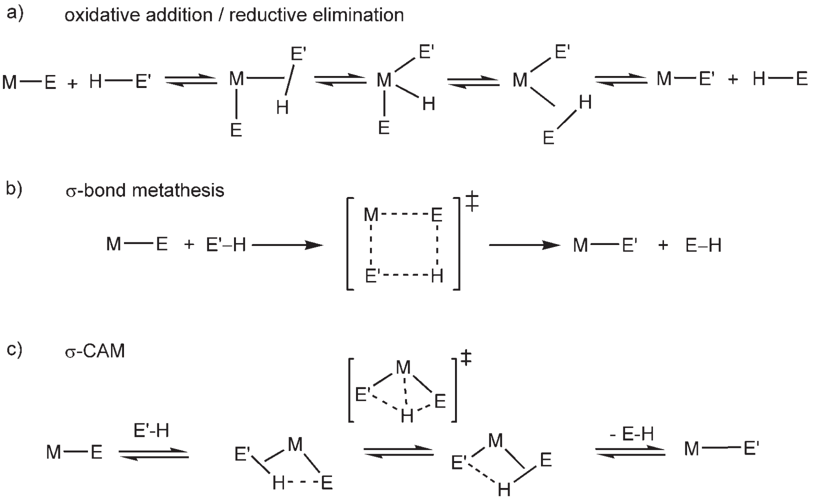
8. Conclusions and Outlook

We have considered three mechanisms for the conversion of M–E to M–E′: oxidative addition/reductive elimination, σ-bond metathesis, and σ-CAM (Scheme 18). The important distinction between classical σ-bond metathesis and σ-CAM lies in the intermediacy of observable σ complexes. Indeed, they may be the starting point of the reactions. Moreover, the σ complexes exhibit well-documented dynamic rearrangements that correspond to a sequence of σ-CAM steps. At this stage, the evidence for σ-CAM mechanisms involving E = H, Si, and B is compelling, and there is increasing evidence for its involvement for E = C, especially with first-row and second-row transition metals. It is expected that those factors that assist the formation of σ complexes will also encourage σ-CAM mechanisms; for instance, metals, electron configurations, and substituents that lead to moderate back donation or an imbalance of forward and back donation.[1]

It is tempting to extend the σ-CAM principle to allow the conversion of coordinated E–H bonds to E–E′ bonds (Scheme 19), but the lack of supporting evidence for σ-E–E′ complexes (E, E′ = B, Si, C) makes this speculative. In 1997, Marder proposed a classical σ-bond metathesis mechanism (as in Scheme 3) for the exchange of boryl ligands in the reaction of $[RhCl(Bcat)_2(PPh_3)_2]$ with $B_2(OR)_4$.[111] Although an intermediate σ-B–B complex could be involved in these



Scheme 17. Mechanism for catalytic borylation of alkanes at {Cp*Rh} species with σ-CAM steps.



Scheme 18. Three fundamental mechanisms for metathesis of M–E a) oxidative addition/reductive elimination; b) σ-bond metathesis; c) σ-CAM.

Scheme 19. A σ-CAM sequence for the reaction of E–E bonds (E ≠ H).

reactions, there is no experimental or theoretical evidence. Similar principles could apply to Si–Si bond formation mediated by late transition metals but again lack mechanistic support.[112–114] In 1992, Tilley et al. had already suggested that "a transient intermediate which may form prior to a four-center transition state is a complex with coordinated Si–H, H–H, or Si–Si σ bonds."[115] There are now a few examples of C–C agostic complexes,[65,116–120] but intermolecular σ-C–C complexes are not known as far as we are aware. We look forward to the discovery of evidence for σ-E–E′ complexes and their reactivity.

The role of σ-CAM mechanisms in catalysis has already been highlighted by DFT calculations on borylation. Similar steps are implicated in hydrogenation and hydrosilation reactions of σ complexes such as $[Ru(H)_2(H_2)_2(PR_3)_2]$. In conclusion, a parallel can be drawn with the reformulation of polyhydride complexes as σ complexes. It is now worth revisiting several stoichiometric reactions and catalytic cycles in the context of σ-CAM mechanisms that offer interesting alternatives to the textbook mechanisms.

The idea of σ-CAM mechanisms invites the question whether π-CAM mechanisms also exist. Indeed, they have been known for many years and are exemplified by the Chauvin mechanism for alkene metathesis.[121–123] More generally, [2+2] cycloadditions at a metal center fit the π-CAM principle. Finally, it should be mentioned that organic molecules can also be transformed at a metal center without coordinating to the metal center directly; such "outer-sphere" mechanisms are now established for transfer hydrogenation.[124–127]

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